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Colloids and Surfaces A: Physicochemical and Engineering Aspects



Salt- and temperature-stable quantum dot nanoparticles for porous media flow



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Gautam C. Kini^{a,1}, Jie Yu^{a,b}, Lu Wang^b, Amy T. Kan^b, Sibani L. Biswal^a, James M. Tour^{c,**}, Mason B. Tomson^{b,**}, Michael S. Wong^{a,b,c,*}

^a Department of Chemical and Biomolecular Engineering, Rice University, 6100 S Main Street, Houston, TX 77005, United States

^b Department of Civil and Environmental Engineering, Rice University, 6100 S Main Street, Houston, TX 77005, United States

^c Department of Chemistry, Rice University, 6100 S Main Street, Houston, TX 77005, United States

HIGHLIGHTS

GRAPHICAL ABSTRACT

- Cadmium selenide nanoparticles (NPs) are colloidally stable in 1 M NaCl brine solution.
- A nonionic ethoxylated alcohol surfactant (Neodol) provides this salt stability.
- NPs are colloidally stable up to 70 °C, near the surfactant cloud point temperature.
- NPs can travel through crushed calcite and sandstone and through a sandstone core.
- NP adsorption during porous media flow can occur due to surfactant clouding.

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ABSTRACT

The transport of colloidal nanoparticles (NPs) through porous media is a well-studied phenomenon at ambient temperature and in low-to-zero salinity water found in aquatic systems. Little is known at much higher temperatures and salinities such as conditions found in petroleum reservoirs, thus limiting the possible use of NPs in downhole oilfield applications. Using 3-nm CdSe quantum dots (QDs) as a model material, we report that NPs can be prepared with excellent colloidal stability at high ionic strengths and elevated temperatures. QDs with an outer coating of a nonionic ethoxylated alcohol surfactant showed little aggregation in synthetic seawater with ionic strength of 0.55 M and 1 M NaCl brine solution based on dynamic light scattering analysis. They showed colloidal stability up to 70 °C, close to the cloud point temperature of the nonionic surfactant. They further showed nearly unimpeded flow behavior when carried in high-salinity water through a packed column of crushed calcite or sandstone mineral at room temperature. QDs were successfully passed through a medium-permeability Berea sandstone core (100 mDa) at 17 atm, 25 °C, and 8 mL/h. The preparation strategy for salt- and temperature-stable QDs is applicable to a wide range of particle sizes and compositions, toward the general handling and use of functional NPs in high-salinity environments.

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* Corresponding author at: Department of Chemical and Biomolecular Engineering, Rice University, 6100 S Main Street, Houston, TX 77005, United States. Tel.: +1 7133483511.

** Corresponding authors.

E-mail addresses: tour@rice.edu (J.M. Tour), mtomson@rice.edu (M.B. Tomson), mswong@rice.edu (M.S. Wong).

¹ Current address: Shell Global Solutions, Westhollow Technology Center, 3333 Highway 6S, Houston, TX 77082, United States.

1. Introduction

The continuing increase in worldwide energy demand has motivated recent efforts of designing nanomaterials with signaling, sensing, and detection capabilities for oil exploration [1–7]. The general objective is to retrieve real-time, spatially resolved physical (e.g., temperature [8–14], pressure [11], rock porosity and permeability [15]) and chemical (e.g., oil [5,6,16,17], water [8,18,19], gas [20,21] and mineral type [22]) information of an oil reservoir after injection of transportable particles. Contrastenhancing agents help detect specific targets at threshold levels and through nanoscale properties, enhance response and resolution of existing X-ray, electromagnetic and seismic-based detection methods [1-4,23-29]. Sensing agents are based on the concept of information gathering via changes in their physical or chemical state during subsurface transport and their subsequent retrieval and analysis [1-5,8,9,13-21,29-34]. There have been recent efforts to fabricate miniaturized electronic devices as sensing agents that measure, store, and communicate reservoir properties [1-4,10-12,17,35-46].

We recently synthesized carbon-based submicron particles with hydrocarbon sensing capability in which a hydrophobic compound is released when transporting through oil-containing rock [5,6]. These "nanoreporters," ~140-nm polyvinyl alcohol-coated carbon particles, flowed rapidly through oil- and non-oil-containing packed columns at room temperature, and with little deposition onto column material. Some aggregation was observed in synthetic seawater after several days, which resulted in partial particle entrapment during flow experiments [5,6]. Partially sulfated polyvinyl alcohol-coated carbon particles were subsequently synthesized, with greatly improved stability to high temperature and salinity [7].

Conditions in an oil reservoir are harsh, with water salinities approaching those of seawater and higher and with temperatures ranging between 70 and 150 °C [1–3]. At oil production sites where water-flooding is used, the salinity can be even higher. A challenging aspect in the design of contrast-enhancing or sensing agents is thus, the need for high colloidal stability in the carrier fluid and under reservoir-relevant conditions. If designed as particles, these agents should also be unaggregated and non-interacting with the reservoir minerals during their transport. Whereas much is known about colloidal stability in low-to-no salt-containing aquatic systems (*i.e.*, below 0.1 M) [47], there are very few studies in which nanoparticles have been specifically designed to be stable in highsalinity water [23,48–50].

Here we report a robust method in preparing salt-stable nanoparticle (NP) suspensions and in assessing their colloidal and transport behavior. Using oleic acid-coated CdSe quantum dots (QDs) as the model NP material, we identified a commercially available nonionic ethoxylated alcohol surfactant to provide water dispersibility. The colloidal stability of the resultant QDs were analyzed through dynamic light scattering at high salinities (synthetic seawater with 0.55 M ionic strength and 1 M NaCl solution) and temperatures up to 70 °C. Transport behavior was assessed by flowing high-salinity suspensions of QDs through calcite and sandstone columns at room temperature and higher temperatures, and analyzing the QD concentrations quantitatively in the effluent. Transport behavior through oil reservoir rock was assessed qualitatively by using Berea sandstone core.

2. Experimental

2.1. Materials

Synthesis of QDs: Oleic acid-coated CdSe QDs were synthesized by the hot injection method following previously published procedures [51,52]. Cadmium oxide (CdO, 99.99%), oleic acid (OA, technical grade – 90%), 1-octadecene (ODE, technical grade – 90%) and trioctylphosphine (TOP, 90%) were all purchased from Aldrich and selenium (Se – 99.99%) was obtained from Strem Chemicals. All chemicals used in this study were used as supplied and without further purification [Caution: Hot injection routes to synthesize QDs involve steps that may lead to hazardous explosive conditions. Please follow necessary safety precautions described in the published procedures].

Phase-Transfer of QDs and Preparation of Aqueous Salt Suspensions of QDs: After synthesis, CdSe QDs were suspended in chloroform (Fischer, ACS grade), to which Neodol 91-7 (Shell Chemicals) was added (referred hereafter as Neodol). The final concentrations were 221 µmol-QD/L-chloroform and 30 mg-Neodol/mL-chloroform. QD transfer from chloroform to water was carried out following a recently published protocol [48]. 1 mL of the QD/Neodol/chloroform solution blend was added to 20 mL of ultrapure water (18.2 M Ω -cm resistivity, pH ~6.8, Barnstead Nanopure Diamond System) to form an emulsion in which QDs solubilized in chloroform, constituted the dispersed phase and water formed the continuous phase. The emulsion was subsequently heated for 30 min at 90 °C so as to boil-off the chloroform (see Supplementary Information Section S1, Fig. S1). As the chloroform evaporated, the hydrophobic carbon chains (tail groups) of Neodol formed bilayers with oleic acid native to the QDs and the hydrophilic ethoxylated head groups project outwards toward water (denoted as QD/Neodol), rendering the QDs water-dispersible

QD/Neodol suspensions (pH 6.6) were diluted in pre-formulated stock solutions of salt so as to form suspensions of QD/Neodol in 1 M NaCl and 0.55 M synthetic seawater. Synthetic seawater is a solution of 3.5 mM CaCl₂, 5.5 mM MgCl₂, 19.8 mM KCl, 0.5 M NaCl, 0.5 mM Na₂SO₄ and 2 mM NaHCO₃[5,6]. The pH value of the final QD/Neodol suspensions in 1 M NaCl and synthetic seawater were 7.8, and 8.5, respectively. All chemicals toward preparing stock solutions were procured from Merck. In all suspensions, the concentration of QDs was $4.5 \,\mu$ M and that of Neodol was $0.75 \,\text{g/L}$. It is to be noted that the phase-transfer of QDs, as reported in our earlier work, could be carried out directly in salt-containing water [48]. However, we found that the benefits of transfer in saltcontaining water (higher phase-transfer yield, transfer of QDs as single-particles) as realized previously with a charged ionic surfactant (Aerosol-OT), diminished when carried out with a nonionic surfactant. Further, losses of salt due to crystallization at high phase-transfer temperature (90 °C) reduced the accuracy of final salt concentrations in the QD suspensions.

2.2. Characterization

Dynamic Light Scattering (DLS): The hydrodynamic diameter of OD/Neodol suspensions in different salt solutions was estimated across temperatures ranging from 6 to 70 °C by DLS. A Brookhaven ZetaPALS DLS instrument, with a BI-9000AT digital autocorrelater, a He–Ne Laser (λ = 656 nm) and a temperature-stabilized sample holder was used for light scattering measurements. Samples were loaded in a stoppered quartz cuvette and pre-equilibrated at a specific temperature for at least 15 min. Sample measurements were made at a fixed scattering angle of 90°, over time intervals of 3 min and repeated at least 5 times for reliable statistics. The measured hydrodynamic diameters were number and volumeaveraged and scattering data were fitted using CONTIN or NNLS fitting routines of the instrument software 9KDLSW. For cases in which D_N and D_V values were equivalent, they were reported as a single D_h value. For cases in which D_N and D_V values were not equal, we observed a bimodal distribution that resulted from the presence of Neodol micelles, as confirmed by analysis of Neodol solutions in respective salinities. In such cases, contributions from

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